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Ferroelectric hysteresis and magnetoelectric effect in orthorhombic $Dy_{1-x}Ho_xMnO_3$ single crystals

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In $Dy_{1-x}Ho_xMnO_3$ single crystals with the orthorhombic space group Pbnm, ferroelectric hysteresis loops were measured for compositions with $x = 0$ and 0.3. As the content of Ho^{3+} ions increases, the hysteresis loop narrows and for $x = 0.3$ it no longer manifests itself. An analysis of the signal corresponding to the hysteretic behavior of a ferroelectric showed that even harmonics can be obtained only if the hysteresis loop is not symmetric about the abscissa axis. In view of the latter, the hypothesis that the second harmonic of the magnetoelectric effect is a consequence of the complex dependence of the polarization on time due to its hysteresis becomes doubtful. Measurements of the dependence of the inverse magnetoelectric effect on the amplitude of the applied electric field $\Delta M(E)$ showed that the first harmonic remains linear with respect to the electric field even in the electric field strength region where the domain structure of the ferroelectric is rearranged.

Keywords: multiferroics, ferroelectricity, hysteresis.

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1. Introduction

Materials in which different ordering types coexist simultaneously, such as magnetic and ferroelectric ordering, as well as spontaneous elastic deformation, are called multiferroics [1]. Much attention is paid to multiferroics due to their potential in spintronics [2–4].

One of the most attractive families of compounds, widely discussed in literature, is the family of orthorhombic manganites with the general formula $RMnO_3$, where R is a rare earth element. A rich pattern of phase transitions is observed in these compounds. When the Neel temperature is reached, the subsystem of Mn^{3+} ions is ordered, however, a rare earth subsystem does not become ordered and is in the paramagnetic state. Depending on rare-earth ion type, various types of $3d$-subsystem ordering are implemented. For instance, antiferromagnetic ordering of the A-type is implemented for $R = La-Eu$ (ordinal numbers $Z = 57-63$), magnetic moments of Mn^{3+} ions have ferromagnetic ordering in the ab-plane and antiferromagnetic ordering along axis c. The antiferromagnetic order of the E-type arises in $HoMnO_3$ ($Z = 67$), when the magnetic structure in the ab-plane is built according to the „up−up−down−down" type [5], which destroys the inversion symmetry in this plane.

For $Z = 65-66$, a series of magnetic transitions arises in manganites with rare earth element Tb and Dy with a temperature decrease. At Neel temperature T_N (41 K for $TbMnO_3$ and 39 K for $DyMnO_3$), an incommensurate sinusoidally modulated collinear antiferromagnetic ordering of magnetic moments of Mn^{3+} ions with wave vector$(0, k, 1)$ arises [6,7].

Spontaneous polarization is not observed in $TbMnO_3$ and $DyMnO_3$ compounds in the sinusoidal magnetic phase. However, with a further temperature decrease, the wave number k decreases up to temperature T_S, below which it remains almost unchanged. A transition accompanied with spontaneous electric polarization along axis c occurs at this point. The ferroelectric phase appears at temperature $T_S = 28$ K for $TbMnO_3$ and 19 K for $DyMnO_3$. The authors of [8] studied the neutron diffraction on a $TbMnO_3$ crystal and showed that magnetic ordering, which corresponds to the ferroelectric phase, is an elliptically modulated cycloidal spiral magnetic structure; this conclusion is also confirmed in [9]. The third magnetic transition is observed at the temperatures of ~ 7 K and ~ 5 K in $TbMnO_3$ and $DyMnO_3$ respectively, and the rare earth subsystem is ordered. The magnetic characteristics were also measured in [10].

Spontaneous polarization below temperature T_S is described by expression $P_\propto \left[(r_{i+1} - r_i) \times [S_i \times S_{i+1}]\right]$, where r_i and S_i is the radius-vector drawn to the i-th ion of Mn^{3+} and its spin respectively [11]. As seen from this expression, polarization is different from zero only when magnetic moments of neighboring Mn^{3+} ions are noncollinear, which corresponds to a spin cycloid. Thereat, the direction of the resulting polarization is perpendicular to direction b

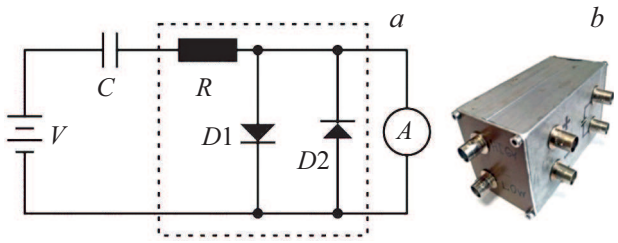

Figure 1. *a* — setup for measurements of ferroelectric hysteresis loops; *b* — switching unit.

of modulation of the magnetic moment and the cycloid plane. Spontaneous polarization along axis c arises in a zero magnetic field in both compounds, that is, the spin cycloid lies in plane bc. However, the application of an external magnetic field in the ab-plane results in a sharp change of the direction of spontaneous polarization $P_c \to P_a$, related to turnover of the cycloid of the Mn^{3+} moments into plane ab. The latter was confirmed experimentally in [12]. The effect of change of direction of the spontaneous polarization vector under an external magnetic field is very attractive, since polarization susceptibility to an external magnetic field at the point of a $P_c \to P_a$ transition is very high and can be of interest for applications.

The switchover of polarization $P_c \to P_a$ is accompanied by the formation of ferroelectric hysteresis loop $P_a(E_a)$, which also means a non-linear dependence of electrical subsystem's response to an external electric field. Since the reverse magnetoelectric effect is caused by an electric field, a nonlinear dependence $M(E)$ can be expected. The present paper deals with a check of this hypothesis and a search for correlations between dependences $P(E)$ and $M(E)$.

2. Experimental procedure

$Dy_{1-x}Ho_xMnO_3$ single crystals with the substitution $x = 0$ and 0.3 were obtained by spontaneous crystallization from solution in the melt. The average size of the obtained single crystals was $\sim 1 \times 1 \times 1.5$ mm. An X-ray diffraction analysis showed that the obtained $Dy_{1-x}Ho_xMnO_3$ single crystals pertain to rhombic space group Pbnm.

For measurements of the reverse magnetoelectric effect and ferroelectric hysteresis loops, the samples were prepared in the shape of plane capacitors by grinding. Coats of epoxy-based current-conducting paste with silver filler were applied on the prepared single crystal faces perpendicular to crystallographic axis a.

The reverse magnetoelectric effect (MEE) was measured using an experimental setup assembled by the authors [13–15].

Ferroelectric hysteresis loops were measured using the setup shown in Fig. 1, *a*. The studied capacitor C in this setup is connected in series with electrometer A (Keithley 6517B) which measures intensity of current flowing through the capacitor and returns the charge after integrating it over time. This setup also contains elements for protection of the electrometer input, resistor R and two antiparallel diodes $D1$ and $D2$. The latter are used to shunt the source voltage in case of breakdown of the studied capacitor and to protect the input cascade from high voltage. Sample C was placed in a helium filled cryostat with a superconducting solenoid of magnetic field with intensity up to 70 kOe.

Fig. 1, *b* shows the switching unit of the setup. Total charge Q flowing through the electrometer was recorded during polarization measurement. A charge can be caused not only by a change of capacitor material polarization, but also by conduction currents, therefore it should be considered as follows:

$$Q = h \int \frac{dP}{dt}\, dt + \int I_R dt. \qquad (1)$$

where I_R is the conduction current related to motion of free charges, $S \cdot dP/dt$ is the current related to a change of capacitor material polarization (S is area formed by one of the capacitor coatings), h is the distance between coatings.

During further processing of measurement results, it was assumed that I_R can be presented as $I_R = k \cdot U$. Then the charge, related to a polarization change, will be found as $q = Q - k \cdot \int U(t) \cdot dt$, where k is the coefficient reflecting the overall conductivity of the setup.

The signal $U(t)$ was shaped using the ± 1000 V voltage source installed on the electrometer. The signal was programmed with linear scanning in time, so that the signal waveform was sawtooth. The hysteretic loop measurement was accompanied by the following voltage change sequence: $0 \to +U \to -U \to +U \to 0$.

3. Results and discussion

An electric field acts on the magnetic subsystem during measurement of the reverse magnetoelectric effect. Let us consider the following variant of magnetoelectric effect formation. An electric field causes sample deformation due to the piezoeffect; the latter causes a change of the crystalline field and exchange interaction between magnetic ions, which eventually results in a change of magnetization, which is the reverse magnetoelectric effect, i.e. dependence of magnetization on external electric field. The sample is a ferroelectric with a hysteresis of polarization by an electric field. In this case, when exposed to an external sinusoidal electric field, a sample will have a piezoelectric deformation, time dependence of which will differ from the sinusoidal law due to polarization hysteresis.

Fig. 2, *a* shows the polarization hysteresis typical for the $DyMnO_3$ compound at 4.2 K in the magnetic field of 60 kOe. This hysteresis was obtained by an approximation of the experimental data given in [7] by function $a \cdot \tanh(E \cdot b - c) + E \cdot d$, where d is the numerical proportionality coefficient. For symmetry, only the upper run of the loop was approximated, and then it was reflected symmetrically in relation to the axis of abscissas. This

dependence was used to restore function $P(t)$, on condition that the electric field is sinusoidal $E = e_0 \cdot \cos(\omega t)$ with the frequency of 100 Hz (Fig. 2, *b*).

The figure shows that dependence of polarization $P(t)$ differs from a sinusoidal one and can be presented as a sum of different harmonics. However, an expansion of this dependence into a Fourier series yields odd harmonics only (Fig. 2, *c*). The latter means that the second harmonic, which is actually recorded in the experiment [15,16], cannot be explained by the polarization hysteresis.

Indeed, the second harmonic can be represented as the result of presence of a term of magnetoelectric effect $1/2\beta E^2$, quadratic in electric field, which does not cross the axis of abscissas E; consequently, this term can result from an expansion into a Fourier series of a signal which is not symmetrical in relation to the axis of abscissas and, therefore, can be explained by hysteretic behavior of polarization. The presence of a time-invariant steady shear also cannot cause the formation of the second harmonic.

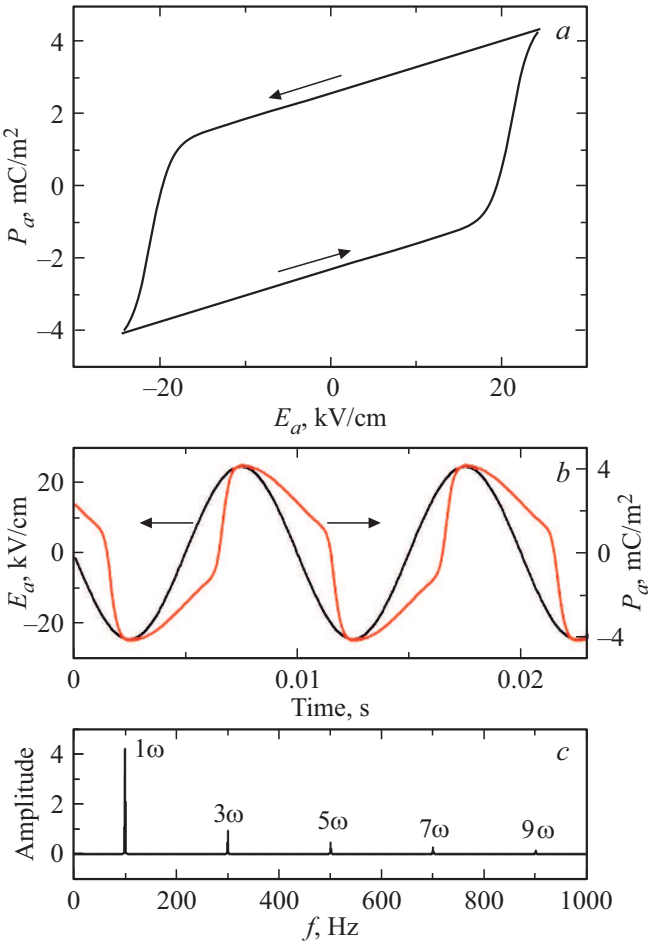

Figure 2. *a* — approximated hysteretic loop of polarization along the *a*-axis in magnetic field $H_b = 60$ kOe, $T = 4.2$ K [7]; *b* — time dependence of polarization, restored according to this loop, upon application of a sinusoidal electric field ($f = 100$ Hz); *c* — values of coefficients of expansion of the received signal $P(t)$ into a Fourier series.

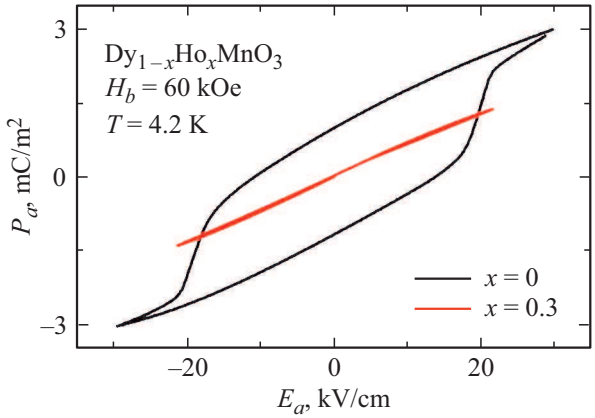

Figure 3. Ferroelectric hysteresis loop of the $Dy_{1-x}Ho_xMnO_3$ samples ($x = 0$ and 0.3) in an external magnetic field $H_b = 60$ kOe at $T = 4.2$ K.

Nevertheless, it can be expected that non-linearity of dependence $P(E)$ of the ferroelectric will lead to non-linear effects in the first harmonic of the magnetoelectric effect $\alpha(H) \cdot E$, since when electric field intensity reaches the values which correspond to readjustment of the ferroelectric domain structure, the non-linear dependence $P(E)$ will manifest itself and, consequently, coefficient α on this area can be dependent on electric field. Therefore, we measured the dependence of the reverse magnetoelectric effect on amplitude of the applied electric field $\Delta M(E)$ in order to find the non-linear dependence of the first harmonic ME_{E}. To make sure that the applied electric field is sufficient for the manifestation of non-linear effects, we measured the loop of ferroelectric hysteresis on a sample of the $DyMnO_3$ single crystal in an external magnetic field $H_b = 60$ kOe at $T = 4.2$ K. The measurement results are shown in Fig. 3. Then the reverse magnetoelectric effect $\Delta M(E)$ was measured on the same sample. As seen from the figure, the region of the most pronounced non-linearity corresponds to the electric field intensity $E_a \approx 20$ kV/cm. With the sample thickness of 0.27 mm this intensity corresponds to 540 V.

Fig. 4 shows the results of measurements of the first harmonic of magnetoelectric effect $\Delta M(E)$ in the magnetic field of 60 kOe at 4.2 K. An alternating electric field with the frequency of 1 kHz was applied to the sample.

The figure shows that dependence $\Delta M(E)$ is well approximated by a linear function, which means absence of dependence $\alpha(E)$, at the least, in the frequency range where the measurements were performed. Indeed, the hysteresis loop shown in Fig. 3 was measured during slow linear scanning of the electric field at a rate of about 2 V/s, while the magnetoelectric effect was measured upon voltage supply to the sample with the frequency of 1 kHz, with a value up to ~ 500 Vrms (the peak value is ~ 700 V). Therefore, the obtained data does not make it possible to unequivocally assert the absence of influence of the ferroelectric hysteretic behavior on the magnetoelectric effect, since the conditions of electric field action differ in

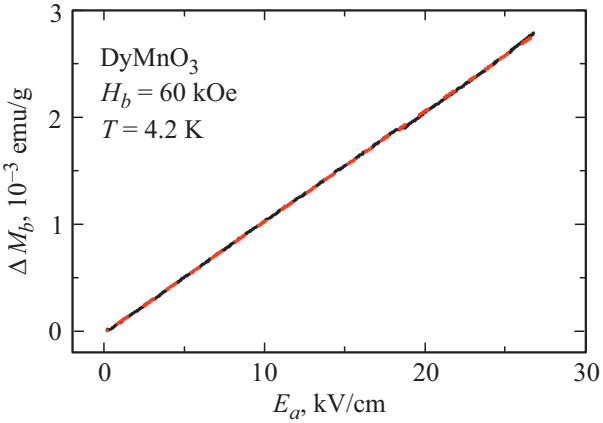

Figure 4. Dependence of the first harmonic of magnetoelectric effect in $DyMnO_3$ on an external electric field, measured at $T = 4.2$ K in the magnetic field $H_b = 60$ kOe.

the experiments. Nevertheless, the authors tend to believe that dependence $\alpha(E)$ is indeed absent in the given range of electric field intensity.

Fig. 3 also shows the measurements of $P(E)$ for the $Dy_{1-x}Ho_xMnO_3$ sample with $x = 0.3$. As the chart shows, the hysteresis for this compound is not observed, meaning the suppression of ferroelectricity as the concentration of Ho^{3+} ions increases; nevertheless, the given compound with $x = 0.3$ still had the weak direct and reverse magnetoelectric effects [16].

4. Conclusion

The measurements of the ferroelectric hysteresis loops for the $Dy_{1-x}Ho_xMnO_3$ compounds with $x = 0$ and 0.3 showed that, as the content of Ho^{3+} ions increases, the hysteretic loop narrows and is not observed for $x = 0.3$. The field, corresponding to readjustment of the domain structure, for $DyMnO_3$ is ~ 20 kV/cm at 4.2 K in the field of 60 kOe. The presence of hysteresis of polarization dependence on electric field $P_a(E_a)$ means that the application of external magnetic field H_b results in a measurement of the direction of spontaneous polarization vector $P_c \rightarrow P_a$. Hysteresis $P_a(E_a)$ does not occur in the absence of a magnetic field.

The performed analysis of the signal, which corresponds to hysteretic behavior of the ferroelectric, showed that an expansion into a Fourier series can yield even harmonics only when the hysteresis loop is asymmetrical in relation to the axis of abscissas. At the same time, odd harmonics arise. These circumstances make dubious the hypothesis that the second harmonic of the magnetoelectric effect is caused by a complex dependence $P(t)$ due to hysteresis $P(E)$, when $E(t) = E_0 \cdot \cos(\omega t)$ is a sinusoidal signal. However, in view of the latter, it is interesting to study the third and other odd harmonics of the magnetoelectric effect in media with hysteresis $P(E)$.

The measurements of dependence of the reverse magnetoelectric effect on amplitude of applied electric field $\Delta M(E)$ have shown that the first harmonic remains linear in relation to the electric field even in the region of readjustment of the ferroelectric domain structure, which against confirms the absence of a direct relation between the reverse magnetoelectric effect and polarization caused by an external electric field.

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Conflict of interest

The authors declare that they have no conflict of interest.

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